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Production of Metallic and Ceramic Parts with the Optoform Process

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ABSTRACT

Optoform LLC developed a technology to process paste compositions based upon photo-curable resins and fillers. This new process is called by Optoform LLC : the direct composite manufacturing. At the present time, about ten alpha machines have been sold in USA and Europe to set up a collaboration between material developers, process developers and end users.

This technique is quite flexible and allows the development of very different material for many different applications. Mainly, four categories of material have been developed, namely soft material, hard material, metallic and ceramic material. Both last kinds will be the main purpose of this presentation.

Metal (316L, 17-4 PH, Titanium) or ceramic (Zircon/Silica, alumina, hydroxyapatite) powders form about 60 % (in volume) of a pasty photo-curable material.

After the building of the prototype on the Optoform machine, a post-processing is required consisting of a debinding and sintering steps. The debinding consists of removing the resin binder by an appropriate thermal treatment. The debinding parameters are a function of the organic phase and of the powder nature.

After that, the part is sintered in order to produce a full dense part and to enhance the mechanical properties. It is also possible to manage a partial sintering to obtain porous parts which can be used when an auto lubricating is needed.

The bimodal distributions of powder and the particules size will be discussed in relationship with the sintering parameters and with the effect on the mechanical properties.

This new process is a development station for new broad range of rapid prototyping (RP) materials and it represents one more step toward the Rapid Manufacturing of high technical parts.

The Optoform process was well adapted to a broad range of applications for parts as well as for shells or Investment casting cores.

1. INTRODUCTION

Originally, Optoform is a French technology which has been bought by 3D systems in 2001. At the present time, about ten alpha machines have been sold in USA and Europe

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This paper will present the material research and the machine development made by the CRIF and other teams (BCRC, KUL, ENSCI).

This technique is quite flexible and allows the development of very different materials such as soft material, hard material, metallic material (stainless steel 316 L or 17-4PH, titanium…) and ceramic material (Zircon/Silica, Alumina and hydroxyhapatite [1]).

One of the main purpose of this conference will be focused on metallic and ceramic materials. Both material kinds require a thermal treatment after processing on Optoform machine. This post-treatment is a debinding and a sintering in order to produce full dense parts or porous ones.

The mechanical properties of the Optoform processed parts are similar to those of parts made by milling.

2. MACHINE PRINCIPLE AND FEATURES

Starting from a 3D file, a part is built on a plateslice by slice from bottom to top. Each succeeding slice is formed by spreading a coating or layer on a plate recovered with a polymer paste which hardens when scanned by a UV laser beam [2]. Figure 1 schematizes the principle of functioning of the Optoform machine.

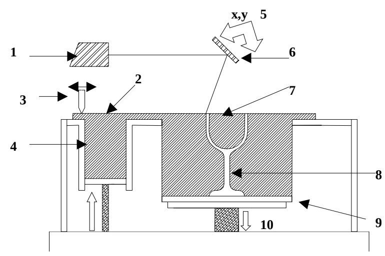

Figure 1 - Optoform principle : 1: UV Laser, 2: Paste supply, 3: recoater including a blade and 2 rotating rods, 4: paste tank, 5: XY rotation, 6: galvanometrical mirror, 7: photosensitive paste, 8: polymerised prototype, 9: building platform, 10: z control.

Because of the scraper stress, supports are needed. The layer thickness is function of the material reactivity to UV and of the application, but it is always in the range of 35 to 120µm. The maximum size of the prototype is 250 x 350 x 500 mm but there are also smaller platforms more suitable to process expensive material or to build small prototypes.

Depending on the geometry of the part and on the material, the building speed is about 25 mm/hour and there is no waiting time during the recoating. Unlike usual stereolithography, the UV scanning is immediate after the passage of the blade.

3. MATERIAL DEVELOPMENT

Every material developed for the Optoform machine must comply with some criteria. Each material includes some resin, some fillers (from 20% up to 70% in volume) and a photo-initiator [3]. In addition, the material could contain rheological agent, thixotropic additives and wetting agent.

The paste must have the firmness of a toothpaste which doesn't flow with gravity. The viscosity and the flow behaviour of the paste follow the Bingham's model. Thanks to the paste consistency, no vat is needed to build a model.

The paste mixture must be stable with time, and the filler should not deposit sediment, and, the fillers has not to absorb the UV light.

Basic curing resins of those materials are generally acrylates, methacrylates or epoxy [3].

In any case, after building, the parts require a cleaning step. A wise choice of solvent, which will dissolve the paste and not the part, is important to the cleaning step.

Some of those materials produce parts which can be used immediately after processing on the Optoform machine. Such it is the case for soft materials which are used to build gaskets. Hard materials allow the building of:

- Shells for injection of thermoplastic materials like polypropylene random polymer and acrylonitrile butadiene styrene (ABS) in a tool
- Tools realisation for silicon and polyurethane-casting
- Shells for wax injection for investment casting
- Thermoforming tools - Sheet metal forming tools

Metallic and ceramic materials require a thermal post-treatment of debinding and sintering.

4. CERAMIC MATERIAL

Original development of ceramic paste compositions compatible with the Optoform device had been carried out at the SPCTS laboratory (ENSCI-Limoges) [7-8]. Optoform LLC is pursuing the development in this field on his own.

The last two years, CRIF and BCRC have also developed Zircon/Silica and Alumina based formulations. The ceramic concentration in the paste is up to 55 (vol) % [9-10].

The ceramic manufacturing also requires debinding and sintering steps which cause a significant shrinkage needing careful management.

The layer thickness can be in the range of 50 to 100µm as a function of the required accuracy in height for the part. The x and y accuracy is limited by the diffraction of the beam due to the ceramic particles. This induces an enlargement of the polymerisation width.

The mechanical properties of Optoform processed ceramic parts are similar valued to those processed using conventional for ceramic processing (pressing).

Some Optoform parts have already been tested as cores in the investment casting process.

CRIF is now developing silicon carbide material. Work to date has employed micron sized particules, but our objective is to develop submicron and perhaps nano-metric, paste material. The debinding and the sintering are performed by INSA of Lyon.

The figure 2 shows greens of small and complex parts (trigger, other mechanism of weapon and a small-scale model of accelerator).

Figure 2: Example of green parts made in SiC

5. METALLIC MATERIAL

Optoform has patented metallic compositions [5-6].

CRIF is also working in collaboration with the KULeuven (Belgium) to develop materials highly filled with metallic powders (60 vol% of metal powder in the paste). The figure 3 shows the homogeneity of the material cured on Optoform. The metallic powder is well dispersed in the photo-curable material. After the building on the Optoform machine, a post-processing is required consisting in debinding and sintering steps. The debinding consists in removing the resin binder by an appropriate thermal treatment. The debinding parameters are a function of the organic phase and of the metallic nature. The most important parameters of debinding are the gas atmosphere (reducing or neutral one), pressure, rate of heating and final temperature.

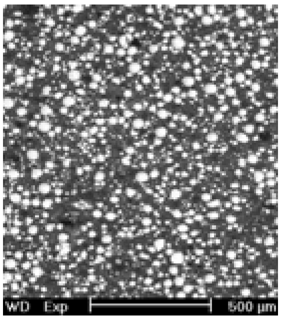

Figure 3. Magnification of 75X. Section in a part curred on Optoform machine. At this step, the part is composed of 60% (Vol) metal and 40% (Vol) resin.

Figure 4. Section in a part of stainless steel after debinding and sintering .

For stainless steel, the residual carbon concentration must be checked. A low residual carbon concentration will induce a sintering at a lower temperature and low mechanical properties (Figure 4). Then, hydrogen atmosphere is not enough efficient to remove all the carbon and to avoid the carbide formation. The following Table 1 illustrates this phenomenon. After the debinding, the sintering is processed in order to produce a full dense metallic part and to enhance the mechanical properties.

Maximum T° of sintering (°C)	Tensile Modulus @ break (MPa)	Elongation @ the break (%)
1360	357	22.5
1380	520	39.9

This is why, CRIF has developed a special binder containing additives which is very efficient in removing organic carbon during debinding. Thanks to those additives the final concentration of carbon is for example about 0.04% for a 316 steel.

It is also possible to manage a partial sintering to obtain porous parts which can be used when auto lubricating on is needed or to decrease the shrinkage of massive parts. In this last case, the prototype must be infiltrated with a metal (brass or lower fusion point metal).

Untill now, the metallic research was mainly dedicated to the 316L, 17-4PH and Mo-alloys for which the powder selection, the debinding and the sintering has been performed. Some processing trials for Titanium models have been planed.

The trials on stainless steel have demonstrated a bimodal distribution of spherical is more adapted to this process. The average particle diameter can be comprised between 16µm and 60µm.

6 CONCLUSIONS

This new process is more than a new Rapid Prototyping technology. It is a development station for a new broad range of RP materials and it represents one more step toward the Rapid Manufacturing of high technical parts.

The Optoform process is well adapted to a broad range of applications for parts as well as for shells.

Materials which can be used directly after Optoform processing or which require post-processing debinding and sintering steps have been developed. The limits or restrictions of use of each type of these materials have been studied in order to meet the requirements and needs of various industrial sectors in the United States and in Europe (e.g. car racing, aerospace and aeronautical sectors, tooling industries, …).

Despite the expensive investment that an Optoform machine represents, this process is first of all, one more step toward the rapid manufacturing.

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MEETING DISCUSSION – PAPER NO: 14

Author: A. Clarinval

Discusser: Unidentified

Question: 1. Do you have isotropic or anisotropic deformation after debinding? 2. Do you expect to produce an Al part by Optoform?

Response: 1. We observe anisotropic deformation of the part driving the sintering of main parts. The shrinkage is about 16% for metallic parts in three directions. For some geometries with alternating massive-non massive areas, some specific supports must be managed during the sintering to avoid deformation. 2: The melting temperature of Al is too close to the debinding temperatures. A perspective way to obtain light parts will be tested soon: First, the part is built in SiC material on Optoform and then debinded. After that, the part (skeleton) is infiltrated with aluminum.

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Production of Metallic and Ceramic parts with the Optoform process

A.-M. Clarinval

Thanks to :

Pr. J.-P. Kruth, Pr L. Froyen and Ms Rombouts from the Katholieke Universiteit van Leuven (KUL – Belgium) for their collaboration in metal debinding and sintering.

J.-P. Erauw and Dr C. Delmotte from the BCRC (Belgium) for their collaboration in the ceramic study.

CRIF

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- Research Institute for the Manufacturing sector in Belgium
- 2450 industrial members
- Objective: Help the companies to improve their competitivity by the implementation of new technologies.
    - Materials Engineering
    - Rapid Manufacturing by additive methods
    - Smart Manufacturing Processes

Optoform?

•**OPTOFORM**: Nancy (France)

Direct Composite Manufacturing Process

•**3DSystems** purchases Optoform (2001)

(technology, machine and material dev.)

•3DSystems + **DSM SOMOS** (materials) >> **OPTOFORM LLC**

•Now : ± **Research machine**.

•**US Partners** : Aerospace, Automotive, Consumer,…

•**EU partners** : CRIF(Belgium), Renault F1 (UK),...

Now : 10 alpha machines

Principle

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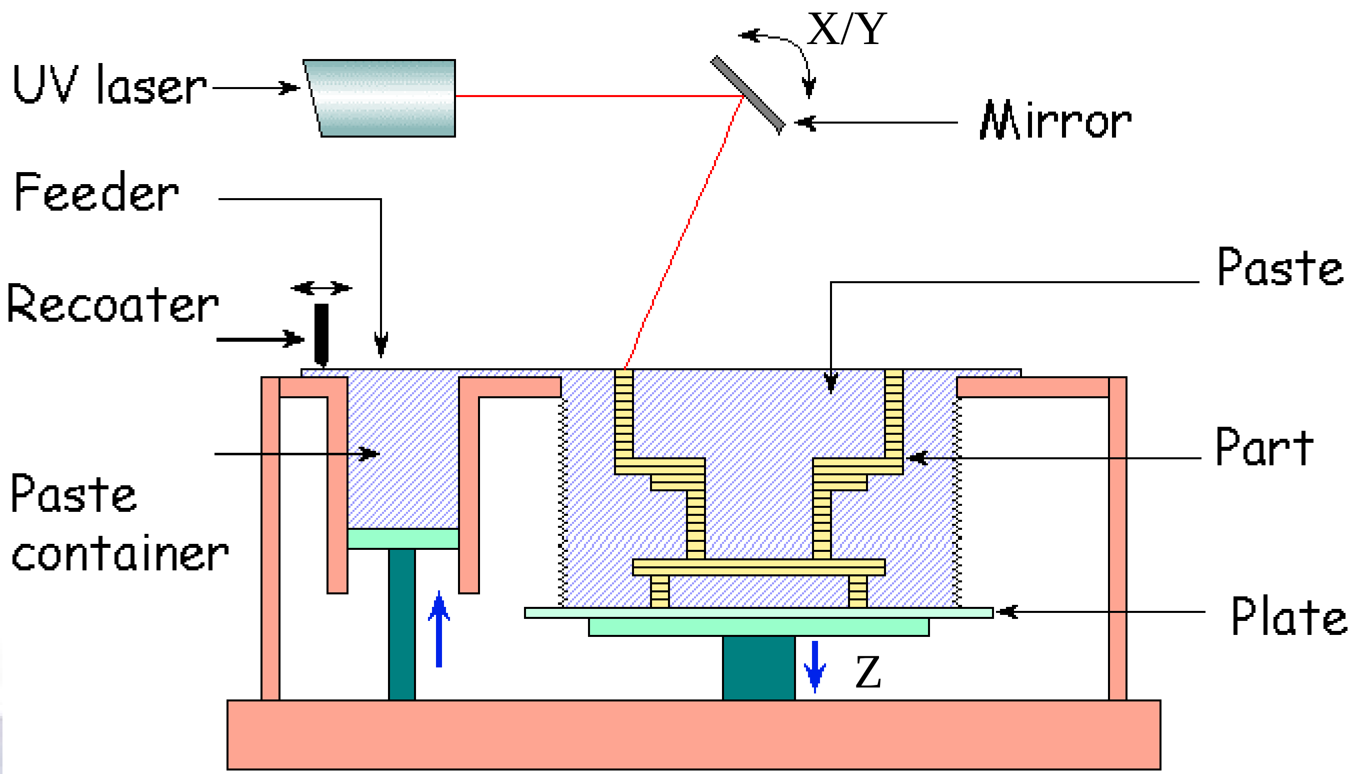

Picture from CTTC (France)

Paste layering and recoating

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Features

- Layer thickness: 20 - 200 µm.
- Argon laser 400-800 mWatts at 351 and 365 nm.
- Max. Size: 250-350-500 mm.
- Several building plates with variable sizes:
  well suited to small parts and expensive materials.
- Supports needed.
- No vat (firmness of the material)

Device Development

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Feeding Modification :

The square piston including a flexible gusset has been changed for :

A more practical system to use (cylindrical + Gasket)

A more chemically resistant system.

Recycling System developed:

A recycling system for the paste

A system to supply the feeding without introducing air pocket or bubbles.

Recoater Modification :

Heavy filled material lift up the blade of 0.28 to 0.30 mm

→ An external device allows to make the blade rigid

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Material Requirements

- Composition :
  Resin+ Fillers (20% to 62% Vol.) + Photo-initiator + Wetting Agent + rheological/ thixotropic Agent
- Consistency : Firmness of a toothpaste (Bingham's model)
- Good Lifetime : the filler should not deposit sediment
- No UV absorbtion by the filler ↔ Layer thickness
- Support removal & cleaning:

  not always easy (isopropanol, water,…).

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4 Categories of materials

1. [Rigid Material: acrylate (CRIF), epoxy (Optoform LLC)]
2. [Soft Material (CRIF)]
3. Ceramics: alumina, zircon/Silica.
4. Metals: stainless steel, titanium.

Debinding+ Sintering

Ceramic Materials (3 systems)

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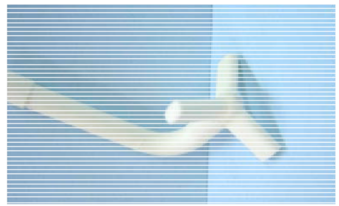
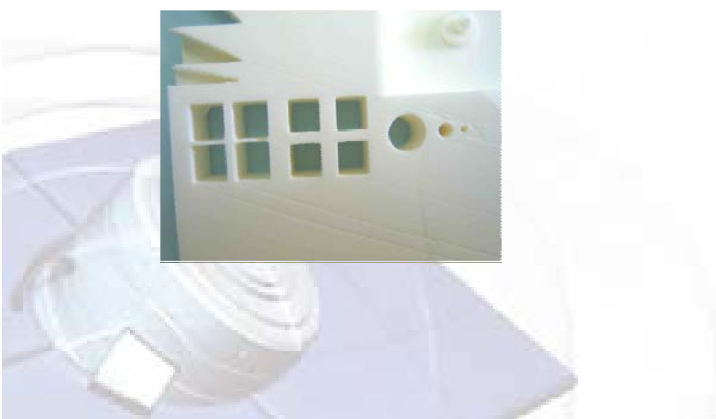
1) Zircon/Silica
2) Alumina
3) SiC





1) Parts are built on Optoform with a paste highly filled;

2) A thermal debinding is performed

3) A full dense sintering is then performed 98%

Ceramics materials

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1) Alumina

1600°C

2) zircon/Silica

1300°C

- Debinding step.
- Sintering (ceramic densification & mechanical properties enhancements) .
- Resolution: diffraction of the beam due to ceramic particles.
- Very thin layers possible: 30-50 µm.
- Mechanical properties: Values identical to conventional techniques for ceramic processing (pressing).

Cores

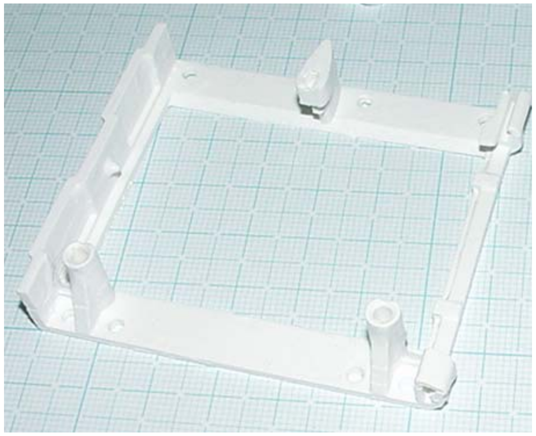
Porosity

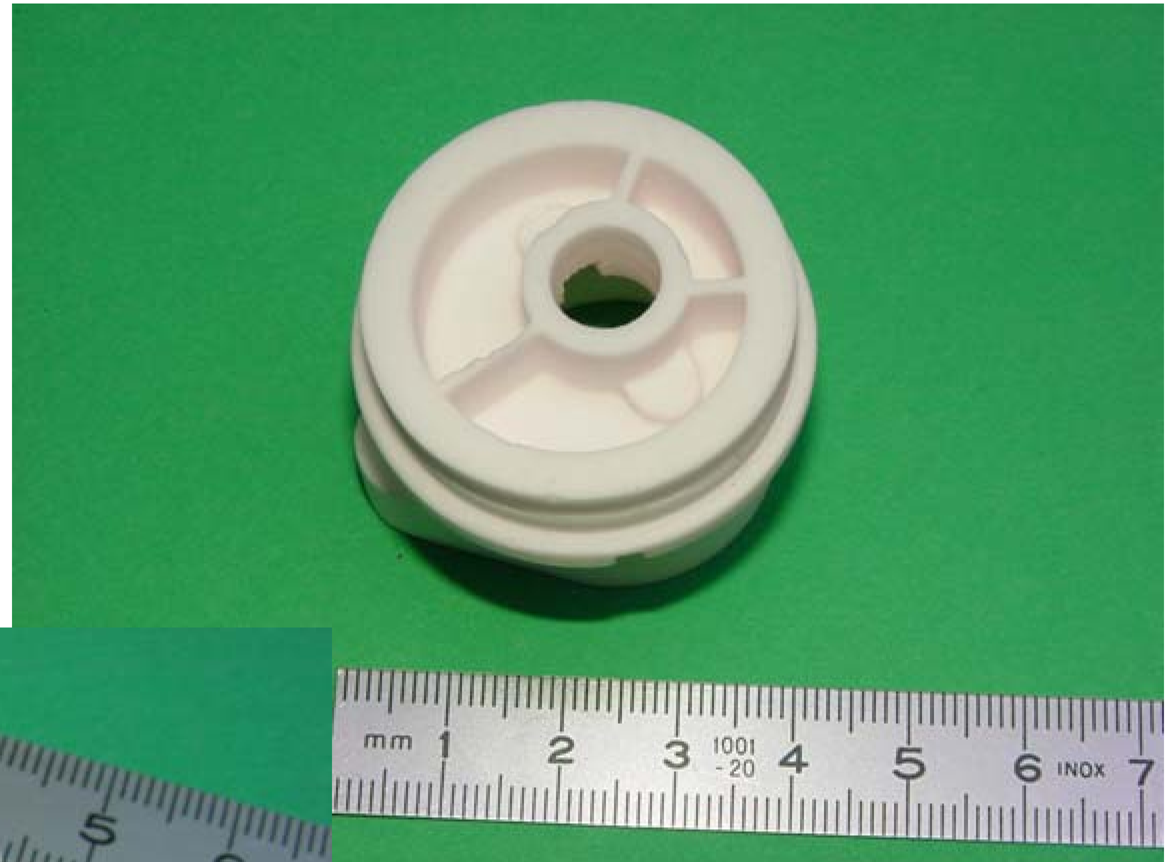
25-30%

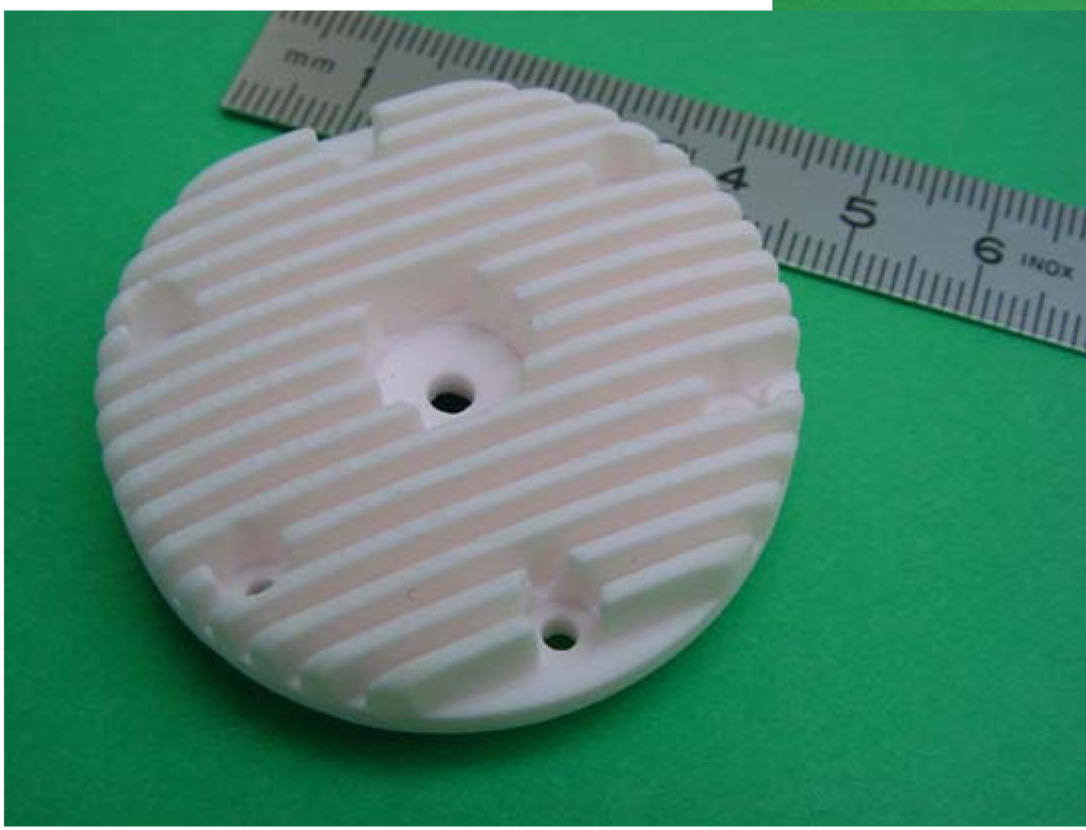
Technical ceramics

Resisting to wear

This research has been realised in collaboration with the BCRC (Belgium)







A few examples

3) Example of SiC parts (green)

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Debinding : ✓

The sintering is improved by the introduction of nano particules

This research is continuing thanks to the EU project : Nanoker

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Metallic materials : Stainless steel

Tricky point : Debinding step (polymer removing)

% C in AISI standaard stainless steel 316 < 0.08 wt%

stainless steel 316L < 0.03 wt%

If reactions between C en Cr occurs during the sintering

- Aloy becomes sensible to corrosion
- Ductility ↓ : (The goal : $\sigma m > 485MPa$; $A > 40\%$)
- Melting point ↓

Metallic materials : Ellingham diagram

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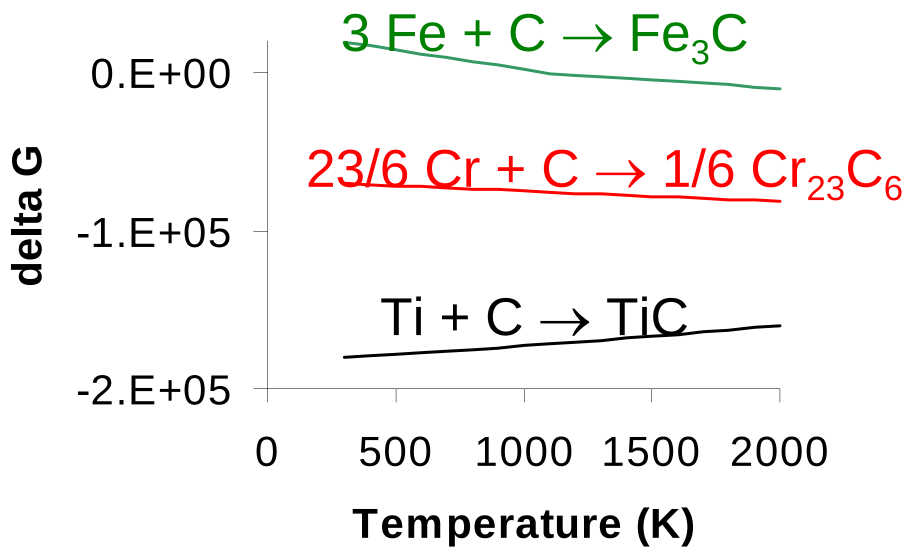
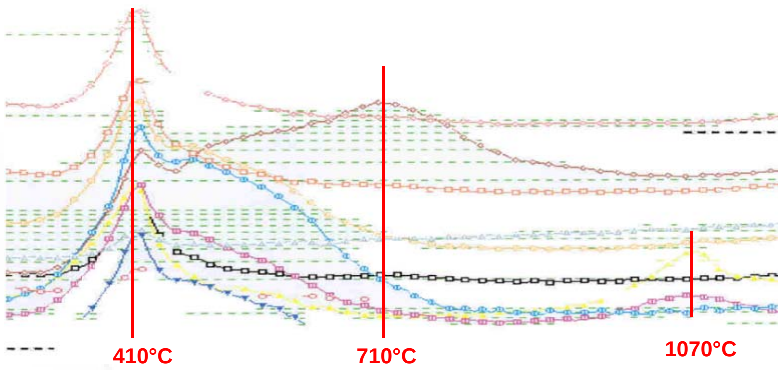


Thermogravimetric study coupled with mass spectroscopy



3 Solutions to avoid the Carbide Formation:

1) Management of the nature of the gases in the furnace
(Reducing atmosphere, H2, CO2 (Boudoir))

2) Addition of small quantities of titanium

3) Addition of specific additives which are eliminated during the debinding

1) Reducing atmosphere : 100% H2

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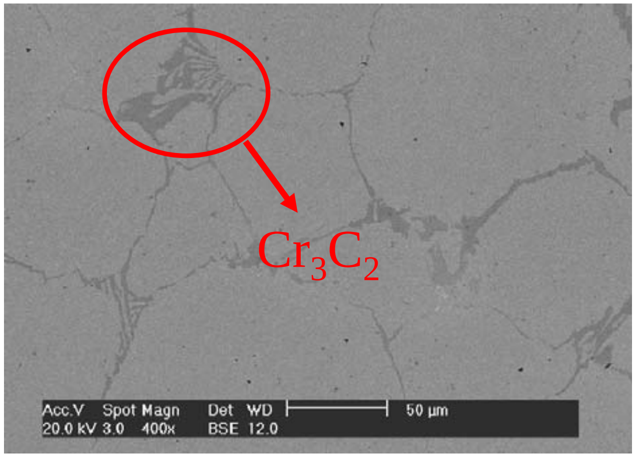

Sintering at 1360°C – 1h
C > 0,17 wt%
σm > 361 MPa; A = 22%

2) Addition of small quantities of titanium

Adding 0,188% of Ti
Sintering at 1360°C – 1h
[C] = 0,043%

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3) Addition of specific additives

For an Alloy rich in Chromium			
	X Anti C2	100% H_2 1360°C	**0.016 ± 0.008**
	X/2 Anti C2	H_2 1360°C	**0.049 ± 0.008**

For an Alloy rich in molybdenium			
	X Anti C3	H_2 1360°C	**0.036 ± 0.008**
	X/2 Anti C3	H_2 1360°C	**0.050 ± 0.008**

Anti C2 and Anti C3 are function of the nature of the alloy and are not changing the chemical composition of this.
A patent is pending.

Metallic Material (mainly : Stainless steel 316L)

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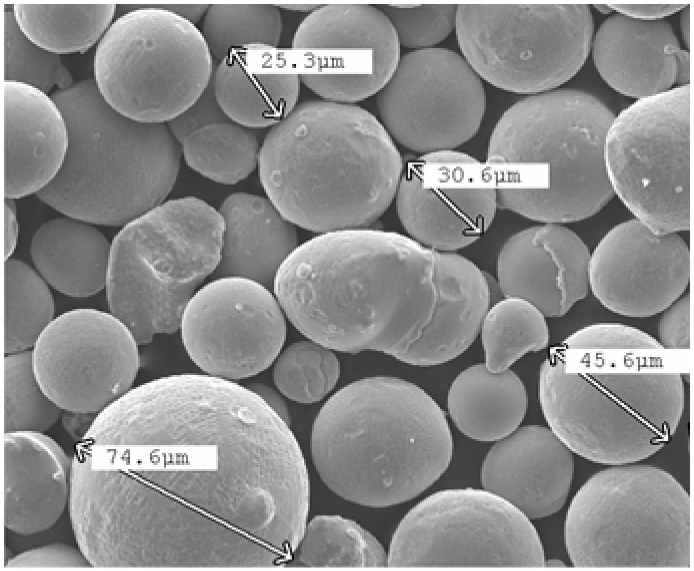
Bimodal distribution of the grain size



Density : 96% - Shrinkage : 16.2%

Summary

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- More than a new RP technology.
- Development station for new RP materials.
- One more step toward Rapid Manufacturing.
- Broad range of ceramic and metallic materials.
- By using a good formulation strategy of the paste, it is possible to respect the chemical composition of the material
- Broad range of applications.
- High speed .
- Suited to small parts and expensive materials as well as massive tools and cheap materials.

I thank you for your attention